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Comparison of Primas  
and Rayleigh-Schrodinger Perturbation Theories

by

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ABSTRACT

The Primas and Rayleigh-Schrodinger formulations of perturbation theory are compared in considerable detail. The Primas approach appears useful only in special cases where the operators involved form a Lie algebra with a small number of elements. For Hamiltonians with degenerate energy levels or for many body systems, the Primas formalism does not appear practical.

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## I. Introduction

This paper is intended as a comparison of the Rayleigh-Schrodinger and the Primas<sup>1,2</sup> formulations of perturbation theory. If taken to infinite order, the two procedures are exactly equivalent. However, if truncated in some finite order, the two formulations give different results. The advantages and disadvantages of each formulation will be discussed, as well as the connections between them. Our viewpoint is somewhat different from that of Robinson who has made some excellent studies of the Primas method.<sup>3,4,5,6,7,8</sup>

The exact Hamiltonian  $H$  and the unperturbed Hamiltonian  $H^{(0)}$  are assumed to each have a complete set of orthogonal eigenfunctions and eigenvalues:

$$H \Psi_n = E_n \Psi_n \quad (1.1)$$

$$H^{(0)} \psi_n^{(0)} = \epsilon_n^{(0)} \psi_n^{(0)} \quad (1.2)$$

It is further assumed that there is a one-to-one correspondence between the unperturbed and the perturbed states of the system and no crossing of levels in going from the unperturbed to the perturbed states. The unperturbed wave functions will be taken to be normalized to unity

$$\langle \psi_n^{(0)} | \psi_n^{(0)} \rangle = 1 \quad (1.3)$$

but the normalization of the perturbed wave functions will be left unspecified at this point. For convenience, it will be assumed that the unperturbed states are all non-degenerate, although the problems resulting from degeneracy will be indicated.

The perturbation operator  $V$  is defined by:

$$V \equiv H - H^{(0)} \quad (1.4)$$

The basic problem of perturbation theory is then to find the exact wave functions  $\Psi_n$  from a knowledge of the unperturbed wave functions  $\psi_n^{(0)}$ . Hence, it is natural to seek an operator  $U^{-1}$  which transforms the unperturbed wave functions into the exact wave functions:

$$\Psi_n = U^{-1} \psi_n^{(0)} \quad (1.5)$$

Equation (1.5) is required to hold for any state  $n$  of the system.

It follows from equation (1.1) that

$$\tilde{H} \psi_n^{(0)} = E_n \psi_n^{(0)} \quad (1.6)$$

where the transformed Hamiltonian  $\tilde{H}$  is defined by

$$\tilde{H} \equiv U H U^{-1} \quad (1.7)$$

The level shift operator  $\mathcal{V}$  is defined by

$$\mathcal{V} \equiv \tilde{H} - H^{(0)} \quad (1.8)$$

From equation (1.6) it is seen that the eigenvalues of  $\mathcal{V}$  are the actual shifts in the energy levels caused by the perturbation:

$$\mathcal{V} \psi_n^{(0)} = (E_n - \epsilon_n^{(0)}) \psi_n^{(0)} . \quad (1.9)$$

The Rayleigh-Schrodinger formulation now follows from expanding  $U^{-1}$  in a power series in a real parameter  $\lambda$  as follows:<sup>1</sup>

$$U^{-1} = 1 + \lambda U^{(1)-1} + \lambda^2 U^{(2)-1} + \lambda^3 U^{(3)-1} + \dots, \quad (1.10)$$

The Primas formulation follows from expanding  $U^{-1}$  in a somewhat different manner:

$$U^{-1} = e^{-i(\lambda S^{(1)} + \lambda^2 S^{(2)} + \lambda^3 S^{(3)} + \dots)} \quad (1.11)$$

These expansions are equivalent as the order becomes infinite, of course, but they differ if the above forms are truncated after some finite order of  $\lambda$ . Each formulation will now be separately considered in greater detail.

## II. Rayleigh-Schrodinger Formulation

### A. Preliminary Remarks

If some of the unperturbed states are degenerate, the expansion in equation (1.10) should actually be

$$U^{-1} = U^{(0)-1} + \lambda U^{(1)-1} + \lambda^2 U^{(2)-1} + \lambda^3 U^{(3)-1} + \dots \quad (2.1)$$

where  $U^{(0)-1}$  is an operator which transforms the zero-order wave functions within each degenerate set to the correct linear combinations

for the treatment of the degenerate problem.<sup>9</sup> Since it is here assumed that the zero-order wave functions are all non-degenerate, we take  $U^{(0)-1} = 1$ .

The operators and functions introduced in Section I are assumed to have power series expansions in  $\lambda$  :

$$\Psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \lambda^3 \psi_n^{(3)} + \dots \quad (2.2)$$

$$E_n = \epsilon_n^{(0)} + \lambda \epsilon_n^{(1)} + \lambda^2 \epsilon_n^{(2)} + \lambda^3 \epsilon_n^{(3)} + \dots \quad (2.3)$$

$$V = \lambda H^{(1)} + \lambda^2 H^{(2)} + \lambda^3 H^{(3)} + \dots, \quad (2.4)$$

$$\mathcal{V} = \lambda \mathcal{V}^{(1)} + \lambda^2 \mathcal{V}^{(2)} + \lambda^3 \mathcal{V}^{(3)} + \dots \quad (2.5)$$

From equation (1.5) it is seen that the perturbed wave functions are given by:

$$\psi_n^{(k)} = U^{(k)-1} \psi_n^{(0)} \quad ; \quad k = 1, 2, 3, \dots, \quad (2.6)$$

and from equation (1.9) it is seen that the perturbed energies are the eigenvalues of the level shift operators:

$$\mathcal{V}^{(k)} \psi_n^{(0)} = \epsilon_n^{(k)} \psi_n^{(0)} \quad ; \quad k = 1, 2, 3, \dots \quad (2.7)$$

### B. The Perturbation Equations

From the defining equation (1.8), the level shift operators are found to be

$$\mathcal{V}^{(1)} = H^{(1)} + U^{(1)} H^{(0)} + H^{(0)} U^{(1)-1} \quad (2.8a)$$

$$\mathcal{V}^{(2)} = H^{(2)} + U^{(1)} H^{(1)} + H^{(1)} U^{(1)-1} + U^{(2)} H^{(0)} + U^{(1)} H^{(0)} U^{(1)-1} + H^{(0)} U^{(2)-1} \quad (2.8b)$$

$$\mathcal{V}^{(k)} = \sum_{m=0}^k \sum_{n=0}^{k-m} U^{(m)} H^{(n)} U^{(k-m-n)-1} \quad (2.8k)$$

Note that since  $UU^{-1} = 1$ , it must be true that

$$U^{(1)} + U^{(1)-1} = 0 \quad (2.9a)$$

$$U^{(2)} + U^{(1)} U^{(1)-1} + U^{(2)-1} = 0 \quad (2.9b)$$

$$\sum_{m=0}^k U^{(m)} U^{(k-m)-1} = 0, \quad (2.9k)$$

The familiar perturbation equations are obtained by applying the operator equations (2.8) to  $\psi_n^{(0)}$  and using equations (2.6), (2.7), and (2.9):

$$(H^{(0)} - \epsilon_n^{(0)}) \psi_n^{(1)} + (H^{(1)} - \epsilon_n^{(1)}) \psi_n^{(0)} = 0 \quad (2.10a)$$



$$(H^{(0)} - \epsilon_n^{(0)}) \psi_n^{(2)} + (H^{(1)} - \epsilon_n^{(1)}) \psi_n^{(1)} + (H^{(2)} - \epsilon_n^{(2)}) \psi_n^{(0)} = 0 \quad (2.10b)$$

$$\sum_{m=0}^k (H^{(m)} - \epsilon_n^{(m)}) \psi_n^{(k-m)} = 0. \quad (2.10k)$$

### C. Intermediate Normalization

The exact wave function in intermediate normalization will be written  $\bar{\Psi}_n$  and the operator which gives  $\bar{\Psi}_n$  from  $\psi_n^{(0)}$  will be written  $\bar{U}^{-1}$ .  $\bar{\Psi}_n$  satisfies equation (1.1) and also the intermediate normalization condition:

$$\langle \bar{\Psi}_n | \psi_n^{(0)} \rangle = 1. \quad (2.11)$$

With the expansion

$$\bar{\Psi}_n = \psi_n^{(0)} + \lambda \bar{\Psi}_n^{(1)} + \lambda^2 \bar{\Psi}_n^{(2)} + \lambda^3 \bar{\Psi}_n^{(3)} + \dots \quad (2.12)$$

it is seen that equation (2.11) implies that

$$\langle \bar{\Psi}_n^{(k)} | \psi_n^{(0)} \rangle = 0 \quad ; \quad k = 1, 2, 3, \dots \quad (2.13)$$

The perturbation equations (2.10) and the normalization requirement (2.11) determine  $\bar{\Psi}_n$  (and hence  $\bar{\Psi}_n^{(1)}$ ,  $\bar{\Psi}_n^{(2)}$ , ...) uniquely except for an overall phase factor which is independent of  $\lambda$ .

The spectral resolutions of the various orders of  $\bar{U}^{-1}$  in this normalization are conveniently written as follows:



$$\bar{U}^{(k)-1} = \sum_m R_m^{(0)} Q_m^{(k)} \mathcal{O}_m \quad ; \quad k = 1, 2, 3, \dots \quad (2.14)$$

where the Hermitian  $R_m^{(0)}$  is the reduced resolvent operator associated with the state  $m$

$$R_m^{(0)} = \sum_{\substack{n \\ (n \neq m)}} \frac{|\psi_n^{(0)} \rangle \langle \psi_n^{(0)}|}{\epsilon_m^{(0)} - \epsilon_n^{(0)}} \quad ; \quad (2.15)$$

where  $Q_m^{(k)}$  is a Hermitian operator introduced and discussed by Hirschfelder:<sup>10</sup>

$$Q_m^{(1)} = H^{(1)} - \epsilon_m^{(1)} \quad (2.16a)$$

$$Q_m^{(2)} = H^{(2)} - \epsilon_m^{(2)} + (H^{(1)} - \epsilon_m^{(1)}) R_m^{(0)} (H^{(1)} - \epsilon_m^{(1)}) \quad (2.16b)$$

$$Q_m^{(k)} = H^{(k)} - \epsilon_m^{(k)} + (1 - \delta_{k,1}) \sum_{s=1}^{k-1} (H^{(k-s)} - \epsilon_m^{(k-s)}) R_m^{(0)} Q_m^{(s)} ; \quad (2.16k)$$

and where  $\mathcal{O}_m$  is a projection operator

$$\mathcal{O}_m = |\psi_m^{(0)} \rangle \langle \psi_m^{(0)}| \quad . \quad (2.17)$$

One cannot usually find the operator  $\bar{U}^{-1}$  itself, which may be applied to any state of the system. Thus, it is customary to focus attention on one particular state, say  $n$ , and attempt to find a wave operator<sup>11</sup>  $W_n$  which is defined so that

$$\overline{\Psi}_n = W_n \psi_n^{(\omega)}. \quad (2.18)$$

From equation (2.14) it follows that

$$W_n = 1 + \sum_{k=1}^{\infty} \lambda^k R_n^{(k)} Q_n^{(k)}. \quad (2.19)$$

Since the wave operator  $W_n$  is only meaningful when it is applied to the function  $\psi_n^{(\omega)}$ , it follows that  $W_n$  (which is by no means unique) can be represented by a function.<sup>12</sup> Thus, Dalgarno and coworkers<sup>13</sup> have had success in expressing

$$\overline{\Psi}_n = (1 + \lambda F_n^{(1)} + \lambda^2 F_n^{(2)} + \dots) \psi_n^{(\omega)}. \quad (2.20)$$

The functions  $F_n^{(1)}, F_n^{(2)}, \dots$  are found by direct integration of the perturbation equations. It is shown in the appendix that if  $H^{(0)}, H^{(1)}, H^{(2)}, \dots$  are real and  $\epsilon_n^{(0)}$  is non-degenerate, then  $F_n^{(1)}, F_n^{(2)}, \dots$  are real functions.

The reaction operator  $t_n$  plays the role of the level shift operator  $\mathcal{V}$  if one considers only the state  $n$ , and is defined by<sup>11</sup>

$$t_n = (H - H^{(0)}) W_n \quad (2.21)$$

so that

$$E_n - \epsilon_n^{(\omega)} = \langle \psi_n^{(\omega)} | t_n | \psi_n^{(\omega)} \rangle. \quad (2.22)$$

#### D. Complete Normalization

The exact wave function in complete normalization will be written  $\hat{\Psi}_n$  and the operator which gives  $\hat{\Psi}_n$  from  $\psi_n^{(0)}$  will be written  $\hat{U}^{-1}$ .  $\hat{\Psi}_n$  satisfies equation (1.1) and also the complete normalization condition

$$\langle \hat{\Psi}_n | \hat{\Psi}_n \rangle = 1. \quad (2.23)$$

With the expansion

$$\hat{\Psi}_n = \psi_n^{(0)} + \lambda \hat{\psi}_n^{(1)} + \lambda^2 \hat{\psi}_n^{(2)} + \lambda^3 \hat{\psi}_n^{(3)} + \dots \quad (2.24)$$

it is seen that equation (2.23) implies

$$\sum_{m=0}^k \langle \hat{\psi}_n^{(m)} | \hat{\psi}_n^{(k-m)} \rangle = 0 \quad ; \quad k = 1, 2, 3, \dots \quad (2.25)$$

The usual set of functions  $\hat{\psi}_n^{(k) \prime}$  which satisfy the perturbation equations and the complete normalization requirement are given in terms of the functions in intermediate normalization  $\bar{\psi}_n^{(k)}$  by

$$\hat{\psi}_n^{(1) \prime} = \bar{\psi}_n^{(1)} \quad (2.26a)$$

$$\hat{\psi}_n^{(2) \prime} = \bar{\psi}_n^{(2)} - \frac{1}{2} \langle \bar{\psi}_n^{(1)} | \bar{\psi}_n^{(1)} \rangle \psi_n^{(0)} \quad (2.26b)$$

$$\hat{\psi}_n^{(3) \prime} = \bar{\psi}_n^{(3)} - \frac{1}{2} \langle \bar{\psi}_n^{(1)} | \bar{\psi}_n^{(1)} \rangle \bar{\psi}_n^{(1)} - \frac{1}{2} \left[ \langle \bar{\psi}_n^{(1)} | \bar{\psi}_n^{(2)} \rangle + \langle \bar{\psi}_n^{(2)} | \bar{\psi}_n^{(1)} \rangle \right] \psi_n^{(0)} \quad (2.26c)$$

However, the functions in complete normalization are not uniquely defined.<sup>14</sup> It may be verified by direct substitution that the functions given by

$$\hat{\Psi}_n^{(1)} = \hat{\Psi}_n^{(1)'} + i a_n^{(1)} \psi_n^{(0)} \quad (2.27a)$$

$$\hat{\Psi}_n^{(2)} = \hat{\Psi}_n^{(2)'} + i a_n^{(1)} \bar{\Psi}_n^{(1)} + [i a_n^{(2)} - \frac{1}{2} (a_n^{(1)})^2] \psi_n^{(0)} \quad (2.27b)$$

$$\hat{\Psi}_n^{(3)} = \hat{\Psi}_n^{(3)'} + i a_n^{(1)} \bar{\Psi}_n^{(2)} + [i a_n^{(2)} - \frac{1}{2} (a_n^{(1)})^2] \bar{\Psi}_n^{(1)} + [i a_n^{(3)} - a_n^{(1)} a_n^{(2)}] \psi_n^{(0)}, \quad (2.27c)$$

where  $a_n^{(1)}, a_n^{(2)}, a_n^{(3)}, \dots$  are arbitrary real numbers, also satisfy the perturbation equations and the complete normalization requirement. Clearly,  $\hat{\Psi}_n'$  is the special case of  $\hat{\Psi}_n$  where  $a_n^{(1)} = a_n^{(2)} = a_n^{(3)} = \dots = 0$ . In fact,  $\hat{\Psi}_n$  differs from  $\hat{\Psi}_n'$  only by a phase factor which is a function of  $\lambda$  :

$$\hat{\Psi}_n = e^{i \{ \lambda a_n^{(1)} + \lambda^2 a_n^{(2)} + \lambda^3 [a_n^{(3)} + \frac{1}{6} (a_n^{(1)})^3 + \frac{1}{2} a_n^{(1)} \langle \psi_n^{(0)} | \hat{\Psi}_n^{(0)'} \rangle] + \lambda^4 \dots \}} \hat{\Psi}_n' \quad (2.28)$$

In complete normalization, it is seen from equations (1.3), (1.5), and (2.17), that the operator  $\hat{U}^{-1}$  is unitary, i.e. that

$$\hat{U}^{-1} = \hat{U}^\dagger. \quad (2.29)$$

From the above discussion, however, it is seen that  $\hat{U}^\dagger$  is not uniquely specified unless the constants  $a_n^{(1)}, a_n^{(2)}, a_n^{(3)}, \dots$  are specified. Following the usual restriction that  $a_n^{(1)} = a_n^{(2)} = a_n^{(3)} = \dots = 0$  (so that  $\hat{\Psi}_n = \hat{\Psi}_n'$ ), the spectral resolutions of the various orders of

$\hat{U}^\dagger$  are given by:

$$\hat{U}^{(1)\dagger} = \sum_m R_m^{(0)} Q_m^{(1)} \sigma_m \quad (2.30a)$$

$$\hat{U}^{(2)\dagger} = \sum_m \left\{ R_m^{(0)} Q_m^{(2)} - \frac{1}{2} \langle \psi_m^{(0)} | Q_m^{(1)} R_m^{(0)} R_m^{(0)} Q_m^{(1)} | \psi_m^{(0)} \rangle \right\} \sigma_m \quad (2.30b)$$

$$\hat{U}^{(3)\dagger} = \sum_m \left\{ \begin{aligned} & R_m^{(0)} Q_m^{(3)} - \frac{1}{2} \langle \psi_m^{(0)} | Q_m^{(1)} R_m^{(0)} R_m^{(0)} Q_m^{(1)} | \psi_m^{(0)} \rangle R_m^{(0)} Q_m^{(1)} \\ & - \frac{1}{2} \langle \psi_m^{(0)} | Q_m^{(2)} R_m^{(0)} R_m^{(0)} Q_m^{(1)} + Q_m^{(1)} R_m^{(0)} R_m^{(0)} Q_m^{(2)} | \psi_m^{(0)} \rangle \end{aligned} \right\} \sigma_m. \quad (2.30c)$$

The analog of the wave operator in complete normalization will be denoted by  $\hat{W}_n$ , which is defined so that

$$\hat{\Psi}_n = \hat{W}_n \psi_n^{(0)}. \quad (2.31)$$

It follows from equations (2.30) that

$$\hat{W}_n^{(1)} = R_n^{(0)} Q_n^{(1)} \quad (2.32a)$$

$$\hat{W}_n^{(2)} = R_n^{(0)} Q_n^{(2)} - \frac{1}{2} \langle \psi_n^{(0)} | Q_n^{(1)} R_n^{(0)} R_n^{(0)} Q_n^{(1)} | \psi_n^{(0)} \rangle \quad (2.32b)$$

$$\hat{W}_n^{(3)} = \left\{ \begin{aligned} & R_n^{(0)} Q_n^{(3)} - \frac{1}{2} \langle \psi_n^{(0)} | Q_n^{(1)} R_n^{(0)} R_n^{(0)} Q_n^{(1)} | \psi_n^{(0)} \rangle R_n^{(0)} Q_n^{(1)} \\ & - \frac{1}{2} \langle \psi_n^{(0)} | Q_n^{(2)} R_n^{(0)} R_n^{(0)} Q_n^{(1)} + Q_n^{(1)} R_n^{(0)} R_n^{(0)} Q_n^{(2)} | \psi_n^{(0)} \rangle \end{aligned} \right\}. \quad (2.32c)$$

The analog of the reaction operator in complete normalization is given by

$$\hat{t}_n = \hat{W}_n^\dagger \hat{H} \hat{W}_n - H^{(0)} \quad (2.33)$$

so that

$$E_n - \epsilon_n^{(0)} = \langle \psi_n^{(0)} | \hat{t}_n | \psi_n^{(0)} \rangle. \quad (2.34)$$

### III. Primas Formulation<sup>1,2,3,15</sup>

This method lends itself most easily to the complete normalization scheme, and hence complete normalization will be used in the remainder of this paper. The method is then characterized by setting

$$\hat{U}^\dagger = e^{-iS} \quad (3.1)$$

where  $S$  is a Hermitian operator, so that

$$\hat{U} = e^{iS} \quad (3.2)$$

and  $\hat{U}^\dagger$  is automatically unitary. It is assumed that  $S$  may be expanded in a power series

$$S = \lambda S^{(1)} + \lambda^2 S^{(2)} + \lambda^3 S^{(3)} + \dots \quad (3.3)$$

Here,  $S^{(1)}, S^{(2)}, S^{(3)}, \dots$  must all be Hermitian operators. A term  $S^{(0)}$  would be added to the right side of equation (3.3) to treat the problems of degeneracy.

Multiplying out the power series which defines the exponential operator  $e^{-iS}$ , the relationships between the Primas operators  $S^{(1)},$

$S^{(2)}, \dots$  and the Rayleigh-Schrodinger operators  $\hat{U}^{(1)\dagger}, \hat{U}^{(2)\dagger}, \dots$  are seen to be given by:

$$\hat{U}^{(1)\dagger} = -iS^{(1)} \quad (3.4a)$$

$$\hat{U}^{(2)\dagger} = -iS^{(2)} + \frac{1}{2}(iS^{(1)})^2 \quad (3.4b)$$

$$\hat{U}^{(3)\dagger} = -iS^{(3)} + \frac{1}{2}iS^{(1)}iS^{(2)} + \frac{1}{2}iS^{(2)}iS^{(1)} - \frac{1}{6}(iS^{(1)})^3; \quad (3.4c)$$

or equivalently:

$$-iS^{(1)} = \hat{U}^{(1)\dagger} \quad (3.5a)$$

$$-iS^{(2)} = \hat{U}^{(2)\dagger} - \frac{1}{2}(\hat{U}^{(1)\dagger})^2 \quad (3.5b)$$

$$-iS^{(3)} = \hat{U}^{(3)\dagger} - \frac{1}{2}\hat{U}^{(2)\dagger}\hat{U}^{(1)\dagger} - \frac{1}{2}\hat{U}^{(1)\dagger}\hat{U}^{(2)\dagger} + \frac{1}{3}(\hat{U}^{(1)\dagger})^3. \quad (3.5c)$$

The level shift operators are given in terms of the Primas operators,  $S^{(1)}, S^{(2)}, \dots$  by

$$\mathcal{V}^{(1)} = H^{(1)} + [iS^{(1)}, H^{(0)}] \quad (3.6a)$$

$$\mathcal{V}^{(2)} = H^{(2)} + [iS^{(1)}, H^{(1)}] + [iS^{(2)}, H^{(0)}] + \frac{1}{2}[iS^{(1)}, [iS^{(1)}, H^{(0)}]] \quad (3.6b)$$



$$\mathcal{V}^{(3)} = \left\{ \begin{aligned} &H^{(3)} + [iS^{(1)}, H^{(2)}] + [iS^{(2)}, H^{(1)}] + \frac{1}{2}[iS^{(1)}, [iS^{(1)}, H^{(0)}]] \\ &+ [iS^{(2)}, H^{(0)}] + \frac{1}{2}[iS^{(1)}, [iS^{(2)}, H^{(1)}]] + \frac{1}{2}[iS^{(2)}, [iS^{(1)}, H^{(0)}]] \\ &+ \frac{1}{6}[iS^{(1)}, [iS^{(1)}, [iS^{(1)}, H^{(0)}]]] \end{aligned} \right\} \quad (3.6c)$$

Equations (3.6) may be regarded as equations which determine  $S^{(1)}$ ,  $S^{(2)}$ , ... Since the commutator of any diagonal operator with  $H^{(0)}$  is zero (in the representation formed by the  $\psi_n^{(0)}$ ), it is clear that the diagonal parts of  $S^{(1)}$ ,  $S^{(2)}$ , ... are not determined by equations (3.6) and hence are arbitrary. It has been customary in the literature to resolve this indeterminacy by requiring that the diagonal part of  $S$  should be zero, i.e. that

$$\langle \psi_n^{(0)} | S | \psi_n^{(0)} \rangle = 0. \quad (3.7)$$

for all states  $n$ .

The arbitrary diagonal elements of  $S$  are related to the arbitrary real numbers  $a_n^{(1)}$ ,  $a_n^{(2)}$ , ..., which were introduced in the discussion of the Rayleigh-Schrodinger formulation. If  $\hat{U}^\dagger$  is specified by

$$\hat{\Psi}_n = \hat{U}^\dagger \psi_n^{(0)} \quad (3.8)$$

then  $a_n^{(1)}$ ,  $a_n^{(2)}$ , ... are given in terms of the matrix elements of the operators  $S^{(1)}$ ,  $S^{(2)}$ , ... by

$$ia_n^{(1)} = \langle -iS^{(1)} \rangle_{nn} \quad (3.9a)$$

$$ia_n^{(2)} = \langle -iS^{(2)} \rangle_{nn} \quad (3.9b)$$

$$ia_n^{(3)} = \langle -iS^{(3)} \rangle_{nn} - \frac{1}{6} \sum_j \sum_k \langle -iS^{(1)} \rangle_{nj} \langle -iS^{(1)} \rangle_{jk} \langle -iS^{(1)} \rangle_{kn} \quad (3.9c)$$

where the off diagonal matrix elements of  $-iS^{(1)}$  are given by

$$\langle -iS^{(1)} \rangle_{jk} = \frac{\langle \psi_j^{(0)} | H^{(1)} | \psi_k^{(0)} \rangle}{\epsilon_k^{(0)} - \epsilon_j^{(0)}}. \quad (3.10)$$

Equations (3.9) demonstrate clearly that the usual convention in the Rayleigh-Schrodinger formulation, that the constants  $a_n^{(1)}, a_n^{(2)}, \dots$  all vanish, is not equivalent to the usual convention in the Primas formulation that the diagonal elements of  $S$  all vanish -- although the conventions are equivalent in the first two orders. The difference, of course, is merely in the choice of phase and hence is not physically significant.

With the convention that  $S$  be off diagonal, the spectral resolutions of various  $S$  operators are given by<sup>16</sup>

$$-iS^{(k)} = \sum_{m \neq n} \sum_n |\psi_m^{(0)} \rangle \langle \psi_m^{(0)}| \frac{\mathcal{V}^{(k)} - [iS^{(k)}, H^{(0)}]}{\epsilon_n^{(0)} - \epsilon_m^{(0)}} |\psi_n^{(0)} \rangle \langle \psi_n^{(0)}| \quad (3.11)$$

for  $k = 1, 2, 3, \dots$  (cf. equations (3.6)).

The Primas approach can be formulated in the domain of a Lie algebra<sup>1,2</sup> (the Rayleigh-Schrodinger cannot). Thus, the operators  $iS^{(1)}, iS^{(2)}, \dots$  arise naturally as the solutions of commutator equations. Formal solutions of such equations are known.<sup>17</sup> For example,  $iS^{(1)}$  satisfies the equation

$$[H^{(0)}, iS^{(1)}] = V^{od} \quad (3.12)$$

where  $V^{od}$  is the off-diagonal part of  $V$ . The off diagonal solution of this equation is

$$iS^{(1)} = -i \lim_{\omega \rightarrow 0^+} \int_0^\infty e^{iH^{(0)}\tau} V^{od} e^{-iH^{(0)}\tau - \omega\tau} d\tau. \quad (3.13)$$

Arthurs and Robinson<sup>4</sup> have demonstrated the use of equation (3.13) in finding  $iS^{(1)}$  for a perturbed linear harmonic oscillator. However, this method of solution does not appear to be practical in most problems of interest.

In some special systems, it is possible to find  $S^{(1)}, S^{(2)}, \dots$  (and sometimes  $S$  itself) by an intuitive use of commutator algebra. This happens when the operators involved form a finite Lie algebra with a small number of elements. Several examples of the use of this method have been reported in the literature.<sup>5,6,7,8,18</sup> As examples, we quote here some results given by Robinson.<sup>6</sup> The perturbations are trivial in each case, as they merely represent changes of scale.

1) Perturbed linear harmonic oscillator:

$$H^{(0)} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} k^2 x^2 \quad (3.14)$$

$$H^{(1)} = x^2 \quad (3.15)$$

$$iS^{(1)} = -\frac{1}{4R^2} \left( 2x \frac{d}{dx} + 1 \right) \quad (3.16)$$

$$iS = -\frac{1}{8R^2} \left\{ \log(1+2\lambda) \right\} \left( 2x \frac{d}{dx} + 1 \right) . \quad (3.17)$$

2) Perturbed hydrogenlike atom:

$$H^{(0)} = -\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{l(l+1)}{r^2} - \frac{Z}{r} \quad (3.18)$$

$$H^{(1)} = \frac{1}{r} \quad (3.19)$$

$$iS^{(1)} = \frac{1}{Z} \left( r \frac{\partial}{\partial r} + \frac{3}{2} \right) \quad (3.20)$$

$$iS = - \left\{ \log \left( 1 - \frac{1}{Z} \right) \right\} \left( r \frac{\partial}{\partial r} + \frac{3}{2} \right) . \quad (3.21)$$

As yet, the operators  $S^{(1)}, S^{(2)}, \dots$  have been found only for relatively simple systems. There does not appear to be any practical method for finding them in complicated problems (e.g. many electron systems).

In the Rayleigh-Schrodinger treatment, a great simplification is achieved by restricting the wave and reaction operators to apply to only one particular state of the system. However, the Primas formulation does not lend itself so easily to such a simplification. If it is desired to replace the Hermitian operators  $S^{(1)}, S^{(2)}, \dots$  with the Hermitian operators  $\mathcal{S}_n^{(1)}, \mathcal{S}_n^{(2)}, \dots$  so that the equation

$$\hat{\Psi}_n = e^{-i(\lambda S^{(1)} + \lambda^2 S^{(2)} + \dots)} \psi_n^{(0)} = e^{-i(\lambda \mathcal{S}_n^{(1)} + \lambda^2 \mathcal{S}_n^{(2)} + \dots)} \psi_n^{(0)} \quad (3.22)$$

is satisfied, then the operators  $\mathcal{S}_n^{(1)}, \mathcal{S}_n^{(2)}, \dots$  must satisfy the following equations:

$$\text{1st order:} \quad \mathcal{S}_n^{(1)} \psi_n^{(0)} = S^{(1)} \psi_n^{(0)} \quad (3.23a)$$

$$\text{2nd order:} \quad \mathcal{S}_n^{(1)} \mathcal{S}_n^{(1)} \psi_n^{(0)} = S^{(1)} S^{(1)} \psi_n^{(0)} \quad (3.23b)$$

$$\mathcal{S}_n^{(2)} \psi_n^{(0)} = S^{(2)} \psi_n^{(0)} \quad (3.23c)$$

$$\text{3rd order:} \quad \mathcal{S}_n^{(1)} \mathcal{S}_n^{(1)} \mathcal{S}_n^{(1)} \psi_n^{(0)} = S^{(1)} S^{(1)} S^{(1)} \psi_n^{(0)} \quad (3.23d)$$

$$\mathcal{S}_n^{(1)} \mathcal{S}_n^{(2)} \psi_n^{(0)} = S^{(1)} S^{(2)} \psi_n^{(0)} \quad (3.23e)$$

$$\mathcal{S}_n^{(2)} \mathcal{S}_n^{(1)} \psi_n^{(0)} = S^{(2)} S^{(1)} \psi_n^{(0)} \quad (3.23f)$$

$$\mathcal{S}_n^{(3)} \psi_n^{(0)} = S^{(3)} \psi_n^{(0)} \quad (3.23g)$$

$$\text{mth order:} \quad \mathcal{S}_n^{(i)} \mathcal{S}_n^{(j)} \dots \mathcal{S}_n^{(l)} \psi_n^{(0)} = S^{(i)} S^{(j)} \dots S^{(l)} \psi_n^{(0)}; \quad i+j+\dots+l=m, \quad (3.23m)$$

The requirements on the operators  $\mathcal{S}_n^{(1)}, \mathcal{S}_n^{(2)}, \dots$  are clearly much more stringent than those on the operators  $\hat{W}_n^{(1)}, \hat{W}_n^{(2)}, \dots$  in the Rayleigh-Schrodinger formulation. Hence, one would expect it to be much more difficult to find satisfactory operators  $\mathcal{S}_n^{(1)}, \mathcal{S}_n^{(2)}, \dots$

Alternatively, one might attempt to replace the Hermitian operators  $S^{(1)}, S^{(2)}, \dots$  by the operators  $\mathcal{A}_n^{(1)}, \mathcal{A}_n^{(2)}, \dots$  where  $\mathcal{A}_n^{(1)}$  is a Hermitian operator of a given form, but  $\mathcal{A}_n^{(2)}, \mathcal{A}_n^{(3)}, \dots$  are not Hermitian. The operator  $-i\mathcal{A}_n^{(1)}$  could not be taken to be a function, say  $f_n^{(1)}$ , since  $f_n^{(1)}$  would then have to be imaginary so as to be antihermitian, while it is shown in the appendix of this paper that, in the most usual circumstances,  $f_n^{(1)}$  must be a real function. Thus,  $-i\mathcal{A}_n^{(1)}$  might be taken to be an antihermitian operator of the form

$$-i\mathcal{A}_n^{(1)} = 2(\nabla f_n^{(1)}) + f_n^{(1)} \nabla \quad (3.24)$$

where  $f_n^{(1)}$  is a real function to be determined from the perturbation equation (2.10a) (the form (3.24) for  $-i\mathcal{A}_n^{(1)}$  is not unique -- third, fifth, seventh, ... derivatives could be used in place of the first derivatives indicated). If the function  $\hat{F}_n^{(1)}$  is known, so that

$$\hat{\psi}_n^{(1)} = \hat{F}_n^{(1)} \psi_n^{(0)} = \left[ 2(\nabla f_n^{(1)}) + f_n^{(1)} \nabla \right] \psi_n^{(0)}, \quad (3.25)$$

then  $f_n^{(1)}$  could be obtained by integration of a first order partial differential equation.<sup>19</sup> The method of characteristics is often useful for this integration.

However, if  $-i\mathcal{A}_n^{(1)}$  is taken to be an antihermitian operator of the form (3.14), then  $-i\mathcal{A}_n^{(2)}$  could not be a purely antihermitian operator. It would have to have a Hermitian part to remove the error in the second order caused by the fact that

$$S_n^{(1)} S_n^{(1)} \psi_n^{(0)} \neq S^{(1)} S^{(1)} \psi_n^{(0)} \quad (3.26)$$

(cf. equation (3.4b)). Even if a satisfactory operator  $S_n^{(2)}$  could be found, it would be even more difficult to find  $S_n^{(3)}$ , since it would be required to remove the errors in the third order caused by  $S_n^{(1)}$  and  $S_n^{(2)}$ . Thus, the difficulties with this method are compounded in each successive order.

#### IV. Approximate Transformations

The Rayleigh-Schrodinger and Primas formulations both give the same transformation  $\hat{U}^\dagger$  in the limit as the order becomes infinite. In practice, however, one must usually be content to solve a problem up through some finite order  $k$ . The two formulations then give different approximate transformations.

In the Rayleigh-Schrodinger formulation (in complete normalization) the approximate operator

$$\hat{U}^{(RS)}(k)^\dagger \equiv 1 + \lambda \hat{U}^{(0)\dagger} + \lambda^2 \hat{U}^{(2)\dagger} + \dots + \lambda^k \hat{U}^{(k)\dagger} \quad (4.1)$$

is not unitary. The most obvious consequence of this is that the corresponding approximate wave function

$$\hat{\Psi}_n^{(RS)}(k) \equiv \hat{U}^{(RS)}(k)^\dagger \psi_n^{(0)} = \left(1 + \lambda \hat{U}^{(0)\dagger} + \lambda^2 \hat{U}^{(2)\dagger} + \dots + \lambda^k \hat{U}^{(k)\dagger}\right) \psi_n^{(0)} \quad (4.2)$$

is normalized only through  $O(\lambda^k)$ . The  $\langle \hat{\Psi}_n^{(RS)}(k) | \hat{\Psi}_n^{(RS)}(k) \rangle$  contains contributions up to  $O(\lambda^{2k})$ , and is not normalized in the



orders  $\lambda^{k+1}$  to  $\lambda^{2k}$ . As Yaris<sup>20</sup> shows, the use of such an unnormalized wave function leads to the appearance of unlinked clusters in expectation values. These unlinked clusters are not physically meaningful (they cancel out in the exact solution as the order becomes infinite) and hence are not desirable in the theory.

The Primas formulation does not suffer from this drawback. The approximate transformation here is given by

$$\hat{U}^{(P)}(R)^\dagger \equiv e^{-i(\lambda S^{(1)} + \lambda^2 S^{(2)} + \dots + \lambda^k S^{(k)})} \quad (4.3)$$

and is clearly exactly unitary. Thus, the corresponding approximate wave function

$$\hat{\Psi}_n^{(P)}(R) \equiv \hat{U}^{(P)}(R)^\dagger \psi_n^{(0)} = e^{-i(\lambda S^{(1)} + \lambda^2 S^{(2)} + \dots + \lambda^k S^{(k)})} \psi_n^{(0)} \quad (4.4)$$

is normalized to unity, and one does not obtain the annoying unlinked clusters.

As a simple example of the different approximate transformations, let us consider again a harmonic oscillator perturbed by  $X^2$  and a hydrogenlike atom perturbed by  $\frac{1}{r}$  (see equations (3.12) - (3.21)). Tables I and II give selected values of the following quantities for the ground states of these systems:

$$E_0^{(\text{exact})} \equiv \langle \hat{\Psi}_0 | H | \hat{\Psi}_0 \rangle \quad (4.5)$$

$$E_0^{(P)}(1) \equiv \langle e^{-i\lambda S^{(1)}} \psi_0^{(0)} | H | e^{-i\lambda S^{(1)}} \psi_0^{(0)} \rangle \quad (4.6)$$

$$E_o^{(RS)}(1) \equiv \frac{\langle \psi_o^{(0)} + \lambda \psi_o^{(1)} | H | \psi_o^{(0)} + \lambda \psi_o^{(1)} \rangle}{\langle \psi_o^{(0)} + \lambda \psi_o^{(1)} | \psi_o^{(0)} + \lambda \psi_o^{(1)} \rangle} \quad (4.7)$$

$$\mathcal{E}_o \equiv \epsilon_o^{(0)} + \lambda \epsilon_o^{(1)} + \lambda^2 \epsilon_o^{(2)} + \lambda^3 \epsilon_o^{(3)} , \quad (4.8)$$

Here  $E_o^{(\text{exact})}$  is the exact energy of the perturbed system.  $E_o^{(P)}(1)$  and  $E_o^{(RS)}(1)$  give the expectation values of the Hamiltonian with the normalized wave function correct through first order in the Primas and Rayleigh-Schrodinger formulations respectively.  $E_o^{(P)}(1)$  and  $E_o^{(RS)}(1)$  are both upper bounds to  $E_o^{(\text{exact})}$  and are both correct through  $O(\lambda^3)$  -- however they differ from  $E_o^{(\text{exact})}$  and from each other in the fourth and higher orders. For purposes of comparison, we also give  $\mathcal{E}_o$ , the energy correct through  $O(\lambda^3)$  but with no contributions from the higher orders ( $\mathcal{E}_o$  is not an upper bound to  $E_o^{(\text{exact})}$ ).

In Tables I and II,  $E_o^{(P)}(1)$  is usually (but not always) closer to  $E_o^{(\text{exact})}$  than is  $E_o^{(RS)}(1)$ . In general, there does not appear to be any a priori way of determining which of  $E^{(P)}(1)$  or  $E^{(RS)}(1)$  will be more accurate. It is further possible that one formulation could give a more accurate approximate expectation value of some operator, but a poorer approximate energy, than the other formulation. Evidently, a backlog of specific examples would be required to make a decision about which formulation should be better in a given problem.

Table I. Energy of the ground state of a perturbed linear harmonic oscillator in atomic units ( $H^{(0)} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} k^2 x^2$  ;  $H^{(1)} = x^2$ ) calculated by four different methods (see equations (4.5) - (4.8)). The results are given for selected values of  $k$  , with  $\lambda = 1$  .

	$E_0^{(exact)}$	$E_0^{(P)}(1)$	$E_0^{(RS)}(1)$	$\epsilon_0$
$k = 0.5$	0.75	6.84	3.25	7.25
$k = 1.0$	0.87	0.96	1.00	1.00
$k = 5.0$	2.598075	2.598079	2.598080	2.598080

Table II. Energy of the ground state of a perturbed hydrogenlike atom in atomic units ( $H^{(0)} = -\frac{1}{2} \frac{\partial^2}{\partial r^2} - \frac{1}{r} \frac{\partial}{\partial r} + \frac{l(l+1)}{r^2} - \frac{z}{r}$  ;  $H^{(1)} = \frac{1}{r}$ ) calculated by four different methods (see equations (4.5) - (4.8)). The results are given for selected values of  $z$  , with  $\lambda = 1$  .

	$E_0^{(exact)}$	$E_0^{(P)}(1)$	$E_0^{(RS)}(1)$	$\epsilon_0$
$z = 1$	0.000	0.068	0.214	0.000
$z = 2$	-0.500	-0.477	-0.421	-0.500
$z = 5$	-8.000	-7.996	-7.985	-8.000

## V. Conclusion

In complicated problems (e.g. many body problems), it would be very difficult to find the operators  $\hat{U}^{(1)\dagger}, \hat{U}^{(2)\dagger}, \dots$  or  $S^{(1)}, S^{(2)}, \dots$ , which may be applied to any state of the system. From a practical standpoint, it is usually necessary to focus attention on one state and find wave and reaction operators which may be meaningfully applied to only that state. This is easily done in the Rayleigh-Schrodinger formulation (where  $\hat{U}^{(1)\dagger}, \hat{U}^{(2)\dagger}, \dots$  are replaced by  $\hat{W}_n^{(1)}, \hat{W}_n^{(2)}, \dots$ ), but, due to the difficulties discussed in Section III, it would be very difficult to do in the Primas formulation (where one would attempt to replace  $S^{(1)}, S^{(2)}, \dots$  by  $\mathcal{S}_n^{(1)}, \mathcal{S}_n^{(2)}, \dots$  or  $\mathcal{A}_n^{(1)}, \mathcal{A}_n^{(2)}, \dots$ ).

The presence of degeneracy in the zero-order states makes it even more necessary to restrict the analysis to one particular level (and so to use the Rayleigh-Schrodinger formulation rather than the Primas formulation). In finding the wave operator  $\hat{W}_n$ , it is only necessary to consider the degeneracy of the state  $n$  under consideration. In the Primas formulation (where it is usually necessary to find the full transformation  $\hat{U}^\dagger$  which may be applied to any state), it would be necessary to give special treatment to all the states which are degenerate in zero order. There may be some mathematical trickery for doing this, but otherwise the Primas approach is definitely not workable for systems with degenerate zero order states.

APPENDIX

We wish to show that the function  $F_n^{(k)}$  which satisfies the equation  $\psi_n^{(k)} = F_n^{(k)} \psi_n^{(0)}$  is a real function if  $H^{(0)}$ ,  $H^{(1)}$ ,  $H^{(2)}$ , ... are real and if  $\epsilon_n^{(0)}$  is non-degenerate.

Proof:

First consider the equation

$$(H^{(0)} - \epsilon_n^{(0)}) \psi_n^{(0)} = 0. \quad (A.1)$$

The fact that  $H^{(0)}$  and  $\epsilon_n^{(0)}$  are real, together with the boundary conditions for acceptable wave functions, insure that the solution of equation (A.1) is unique, aside from the normalization. With the requirement that  $\psi_n^{(0)}$  have unit norm, it may be written as

$$\psi_n^{(0)} = e^{i\delta} \phi_n^{(0)} \quad (A.2)$$

where  $\phi_n^{(0)}$  is a real function which is a solution of (A.1) and has unit norm, and  $\delta$  is a real number independent of  $\lambda$ .

The solution  $\psi_n^{(1)}$  to the equation

$$(H^{(0)} - \epsilon_n^{(0)}) \psi_n^{(1)} + (H^{(1)} - \epsilon_n^{(1)}) \psi_n^{(0)} = 0 \quad (A.3)$$

may be written as

$$\psi_n^{(1)} = (R_n^{(0)} Q_n^{(1)} + C_n^{(1)}) \psi_n^{(0)}, \quad (A.4)$$

where  $C_n^{(1)}$  is a complex number which is determined by the normalization requirement on  $\psi_n^{(1)}$ .<sup>10,14</sup> Thus, the function  $F_n^{(1)}$  which satisfies

$$\psi_n^{(1)} = F_n^{(1)} \psi_n^{(0)} \quad (\text{A.5})$$

may be expressed as

$$F_n^{(1)} = \frac{(R_n^{(0)} Q_n^{(1)} + C_n^{(1)}) \psi_n^{(0)}}{\psi_n^{(0)}} = \frac{R_n^{(0)} Q_n^{(1)} \phi_n^{(0)}}{\phi_n^{(0)}} + C_n^{(1)}. \quad (\text{A.6})$$

Both  $R_n^{(0)}$  and  $Q_n^{(1)}$  are real, so the first term on the right side of equation (A.6) is real. In intermediate normalization,  $C_n^{(1)} = 0$ , while in complete normalization (setting  $C_n^{(1)} = C_n^{(1)}(\text{real}) + iC_n^{(1)}(\text{imag.})$ )  $C_n^{(1)}(\text{real}) = 0$  but  $C_n^{(1)}(\text{imag.})$  is arbitrary (cf, equation (2.27a)) and so can be taken to be zero. In either case,  $F_n^{(1)}$  is then clearly real.

The function  $\psi_n^{(k)}$  may be written

$$\psi_n^{(k)} = (R_n^{(0)} Q_n^{(k)} + C_n^{(k)}) \psi_n^{(0)} + C_n^{(k-1)} \psi_n^{(1)} + C_n^{(k-2)} \psi_n^{(2)} + \dots + C_n^{(1)} \psi_n^{(k-1)} \quad (\text{A.7})$$

where the constants  $C_n^{(1)}, C_n^{(2)}, \dots$  are determined by the normalization.<sup>10</sup> In intermediate normalization, all the  $C_n^{(i)}$  are zero. In complete normalization (setting  $C_n^{(i)} = C_n^{(i)}(\text{real}) + iC_n^{(i)}(\text{imag.})$ ), the  $C_n^{(i)}(\text{real})$  are not necessarily zero, but the  $C_n^{(i)}(\text{imag.})$  (which are arbitrary) may be taken to be zero. Thus, in either normalization we may take  $C_n^{(i)}$ ,  $i = 1, 2, \dots, k$ , to be real.

For the purposes of an inductive proof, we assume that the function  $F_n^{(1)}, F_n^{(2)}, \dots, F_n^{(k-1)}$  are all real functions. Then  $\psi_n^{(k)}$  may be

written

$$\psi_n^{(k)} = \left( R_n^{(\omega)} Q_n^{(k)} + c_n^{(k)} + c_n^{(k-1)} F_n^{(1)} + c_n^{(k-2)} F_n^{(2)} + \dots + c_n^{(1)} F_n^{(k-1)} \right) \psi_n^{(\omega)} \quad (\text{A.8})$$

The function  $F_n^{(k)}$  which satisfies

$$\psi_n^{(k)} = F_n^{(k)} \psi_n^{(\omega)} \quad (\text{A.9})$$

may then be written

$$F_n^{(k)} = \frac{\left( R_n^{(\omega)} Q_n^{(k)} + c_n^{(k)} + \sum_{i=1}^{k-1} c_n^{(k-i)} F_n^{(i)} \right) \psi_n^{(\omega)}}{\psi_n^{(\omega)}} = \frac{\left( R_n^{(\omega)} Q_n^{(k)} + c_n^{(k)} + \sum_{i=1}^{k-1} c_n^{(k-i)} F_n^{(i)} \right) \phi_n^{(\omega)}}{\phi_n^{(\omega)}} \quad (\text{A.10})$$

All terms on the right side of (A.10) are real, and so  $F_n^{(k)}$  is a real function.



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